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EFFECT OF PdO ON TiO_2 LOADING ON CHEMOCHROMIC DETECTION OF HYDROGEN

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Abstract

Safety is always a concern in all applications that utilize hydrogen (H_2) in one form or the other. Hydrogen leaks are invisible and odorless. In addition, blending odorants or additives into hydrogen in a manner similar to natural gas is generally undesirable for certain applications including proton exchange membrane fuel cells. To facilitate detection of the location of hydrogen leaks, a special chemochromic H_2 sensing material that employs titania (TiO_2) supported palladium oxide (PdO) pigments encapsulated within a special silicone matrix has been developed at the Florida Solar Energy Center (FSEC). Several batches of PdO H_2 sensing pigments were synthesized using various TiO_2 supports and their hydrogen detection activity determined. TEM and Particle size distribution analysis showed that smaller particles with hemispherical crystalline structure produced faster coloration kinetics when exposed to H_2 gas. However, uniformly distributed PdO particles on the TiO_2 surface displayed greater color contrast, quantified by ΔE measurements. XRD analysis indicated that the crystalline phase of TiO_2 had no effect on the chemochromic performance of the pigments in laboratory environment.

1. Introduction

Hydrogen (H_2) is a prospective energy carrier poised to replace fossil-based transportation fuels. Currently, H_2 is the primary fuel of today's space vehicles (*e.g.*, rocket motors). It is also used in fuel cells that generate electrical power. Furthermore, hydrogen is an important chemical commodity produced and used in many industries. For example, it is used for the reduction of metal oxides (*e.g.* iron ore), ammonia synthesis, and production of hydrochloric acid, methanol and higher alcohols, aldehydes, hydrogenation of various petroleum, coal, oil shale and edible oils, among others. One key issue in all hydrogen related applications is operational safety. Hydrogen is a colorless, odorless gas with a lower explosive limit of about 4% in air. Therefore, reliable and rugged sensors are required to detect hydrogen leaks wherever it is produced, stored, or utilized. There are many point-of-use electronic sensors available for detecting hydrogen leaks in both transfer lines and storage sites. For example, sensors that consist of a palladium alloy are in service for detecting H_2 leaks during pre-launch activities of the space vehicles. One of the concerns regarding these sensors is the requirement of a high operating temperature (greater than 200°C) and elevated temperatures (greater than 500°C) to reactivate the sensing

element. Another issue is sensitivity of the sensing element to other gases in the ambient including water vapor, various hydrocarbons and reducing gases such as carbon monoxide and hydrogen sulfide.

Although not conventionally used, chemochromic detectors for hydrogen sensing have also been known. For example, a tungsten oxide or vanadium oxide layer coated with a palladium layer has been used for optical detection of low concentration of hydrogen gas.[1,2] These sensors lack field stability and have a tendency to crack and peel, and can be washed off by precipitation and/or condensation. Thus, there is a need for an improved, reliable and rugged hydrogen sensor that can operate in a variety of applications (*e.g.* space travel, land transportation, oil refineries, ammonia plants, hydrogen liquefaction plants, etc.).

In this paper, we describe the development of a simple and robust hydrogen sensing material that can be readily applied to the surface of the hydrogen transport pipes, flanges, joints and all places that may encounter the possibility of the hydrogen gas leaks. The technique provides a visual method for detection and location of the H_2 leaks especially during hazardous handling and operations as it does not require any power or operator presence. This is especially important during H_2 transportation, loading, and storage due to the low flammability limit of hydrogen.

Titania (TiO_2) supported PdO hydrogen-sensing pigments described in this work were mixed with a silicone matrix and cast as tapes. When the pigment is exposed to H_2 gas, PdO is reduced to Pd resulting in a color change from beige to dark gray. While titania support does not change color, it does play an important role in the chemochromic reaction, as the type of the TiO_2 used affects the function of the pigment.[3] This paper presents the experimental results for the effect of PdO particle size and distributions over TiO_2 on the overall chemochromic behavior of the hydrogen sensing pigments.

2. Experimental

Pigments Preparation. The pigments are based on PdO supported on TiO_2, which undergoes a color change when contacted with hydrogen.[4] Several chemochromic pigments were synthesized using four different TiO_2 support materials: Aldrich titania (mainly, rutile crystalline form) with an average particle size of 1 micron, Fisher Scientific TiO_2, DuPont R103 TiO_2, and Degussa P25 nanosize TiO_2.

Tape Preparation. The chemochromic hydrogen sensing tape was a mixture of 3-wt% of pigment in a silicone matrix. The thickness of the tape was varied during production. Typically, the mixture was spread into thin films (approximately 2 mils) using a Gardco adjustable film applicator on wax paper.

Transmission Electron Microscopy (TEM). An FEI/Philips, Tecnai F30, 300 kV field emission source TEM instrument, equipped with STEM, HAADF detector and XEDS was used to perform TEM bright field high resolution imaging analysis. The software used was Tecnai G2 Digital Micrograph (DM) and Tecnai Imaging & Analysis (TIA). Samples were mounted on a micro-grid by placing a few droplet of a methanolic suspension of pigment, followed by air-drying.

X-ray Diffraction (XRD). The crystalline phase of the TiO_2 particles was analyzed by means of Rigaku XRD using a CuK_α radiation at 40kV from 20° to 70° at a rate of $2°min^{-1}$ (2θ).

Color Change Measurements. A ColorTec-PCM colorimeter was used to measure pigments color change before and after exposure to hydrogen gas.

3. Results and Discussions

3.1. *Pigments' Responses to Hydrogen Exposure*

As previously noted, the chemochromic hydrogen sensing pigments are based on titania supported PdO. When the pigment is exposed to hydrogen gas, PdO is reduced to elemental Pd resulting in a color change from beige to dark gray. Since it is difficult for the human eye to quantitatively detect the intensity of color change, a colorimeter was employed that incorporated an algorithm capable of quantifying the color change, ΔE, using following parameters: L- lightness value, a- position on red-green axis, and b- position on yellow-blue axis.

$$\Delta E = \{(L-L')^2 + (a-a')^2 + (b-b')^2\}^{1/2} \qquad (2)$$

Eqn. **2** gives a standard measurement with which to compare the color change associated with different samples. The larger is the ΔE value, the greater is the color contrast. The chemochromic films were analyzed before and after exposure to hydrogen gas, allowing quantification of the extent of color change.

Each pigment formulation was exposed to hydrogen in an exposure chamber and analyzed at specific time intervals. Samples were analyzed with the colorimeter to obtain the corresponding ΔE value. Figure 1 depicts the ΔE values vs. hydrogen exposure time for four different titania supports in the TiO_2/PdO pigments. All pigments started to change color after 1.5 minutes of exposure time except Degussa P-25 based pigment, which began changing color almost immediately after exposure to H_2 gas. The pigment based on Aldrich TiO_2 demonstrated the highest value of ΔE (= 38) after 3 minutes of exposure time, while other pigments reached ΔE values no more than 26 for the same length of exposure time.

3.2. *XRD*

Most TiO_2 photocatalysts contain anatase crystalline phase.[5] Anatase titania has a band gap of 3.2 eV while rutile TiO_2 has a band gap of 3.0 eV. Rutile TiO_2 has limited photocatalytic activity. It is known that Degussa P-25 is a mixture of these two phases with an approximate composition of 75% anatase and 25 % rutile phase (Figure 2b). Aldrich and DuPont R103 TiO_2 are mainly rutile (Figure 2a). Fisher TiO_2 was the only sample with unknown crystalline phase. The crystal structure of Fisher TiO_2 was characterized using XRD and the diffraction pattern is given in Figure 2c. The sharp peaks at 25.3° and 47.9° were attributed to anatase TiO_2.[6-9] These results indicate that photocatalytic activity of TiO_2 or lack thereof has no effect on the chemochromic activity of TiO_2/PdO pigments in laboratory environment.

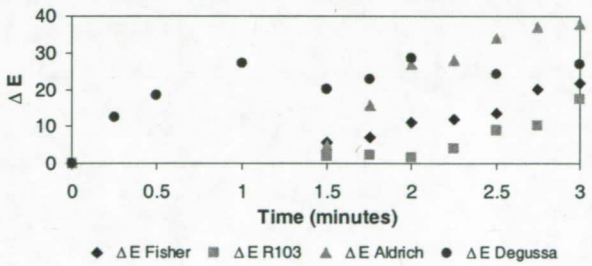

Figure 1. ΔE vs. exposure time to H_2 for four different titania supports in TiO_2/PdO pigments.

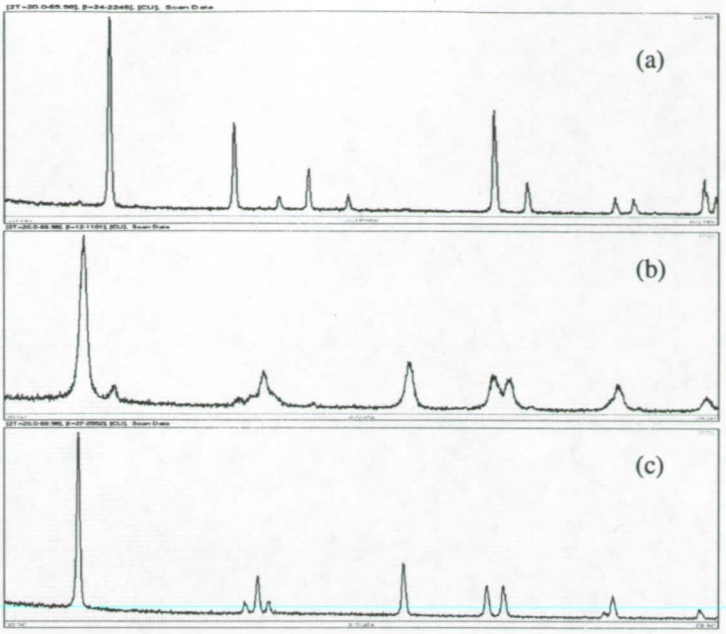

Figure 2. XRD Spectra of TiO_2 supports (a) Aldrich, DuPont R103, (b) Degussa P-25, and (c) Fisher.

3.3. *PdO/TiO_2 Particle Characterization*

To obtain information on the size and morphology of the pigments and to explore the underlying chemistry and role of the TiO_2 support in the coloration reaction, the pigments were subjected to a detailed transmission electron microscopic study.[7,8]

Figure 3 shows TEM images of various PdO/TiO_2 pigments using different titania supports. Although all pigments had been synthesized in the same manner, nonetheless it can be seen that the size of PdO particles and distribution vary considerably. PdO particles are clearly visible as dark colored areas on the surface of the TiO_2 particles. In the case of Degussa P-25 and Aldrich TiO_2, the hemispherical PdO crystallites were well dispersed and strongly attached to the metal oxide support at their flat planes (Figures 3A-D).[7]

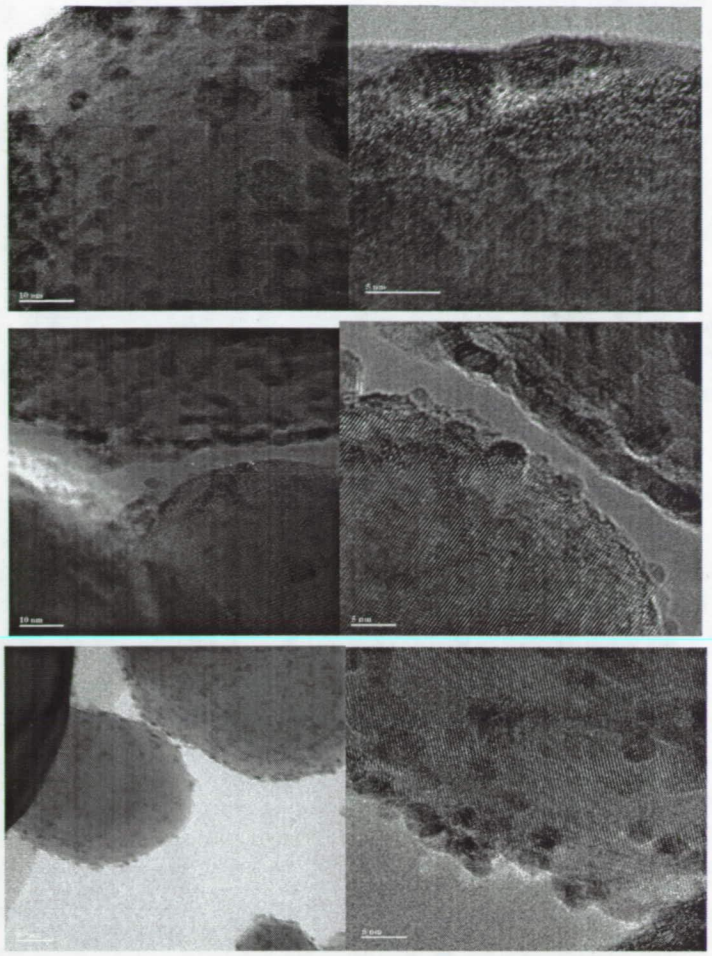

Figure 3. TEM images of (A-B) PdO/Degussa P-25 TiO_2, (C-D) PdO/Aldrich TiO_2, (E-F) PdO/Fisher TiO_2, and (G-H) PdO/DuPont R103 TiO_2 pigments.

Faster response time of Degussa P-25 based pigments compared to that of Aldrich could be explained in terms of the size and homogeneity of PdO particles and their interaction with TiO_2 surfaces. The PdO particle size for Degussa P-25 was homogenous with an estimated mean particle diameter of 2.0 nm. On the other hand, the size of the PdO particles on the Aldrich TiO_2 was less homogenous and varied from 2 to 10 nm with an estimated average particle size of 3.4 nm. Figure 4 depicts the PdO particle size distribution on various titania supports tested. Results of Figure 4 imply that the one overwhelming difference between Aldrich based pigments with others is the wide size distribution of PdO particles.

Fisher and DuPont R103 supported pigments (Figure 3E-H) gave similar results when exposed to hydrogen gas. In both cases, PdO particles were more spherical and as a result had less interaction with the TiO_2 support surface compared to Degussa P-25 and Aldrich supported pigments. Mean Diameter of PdO particles for Fisher and DuPont R103 pigments were larger than 3.1 nm and 2.5 nm, respectively.

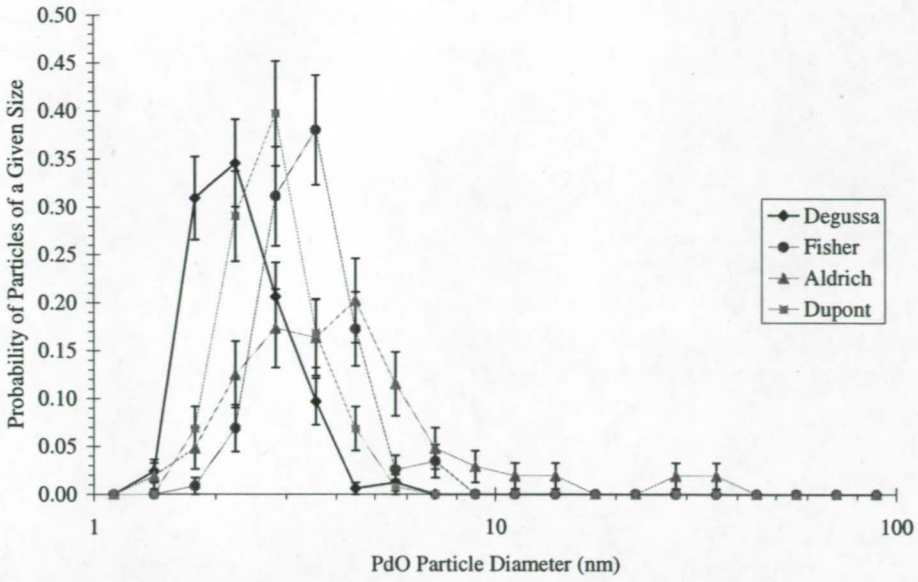

Figure 4. PdO particle size distribution on various titania support.

4. Conclusions

Four different chemochromic TiO_2 supported PdO pigments were synthesized and their activity toward hydrogen was measured. Degussa P-25 based pigments yielded the fastest discoloration kinetics toward H_2 gas while the Aldrich titania (mainly rutile crystalline form) based pigments had the greatest ΔE, color contrast, value. The chemochromic activity of the pigments toward hydrogen is a strong function of the particle size and level of PdO dispersion on theTiO_2 support surface. Smaller PdO_particles with hemispherical crystalline structure produced faster kinetics when exposed to H_2 gas. However, more uniformly distributed PdO particles on the surface of TiO_2 gave larger color contrast number, ΔE. XRD analyses show that TiO_2 crystalline phase apparently had no_effect on the chemochromic performance of these pigments in laboratory environment.

Acknowledgements

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